

DERWENT-ACC-NO: 1994-354776

DERWENT-WEEK: 200282

COPYRIGHT 1999 DERWENT INFORMATION LTD

TITLE: Prepn of alkyl acrylate! polymer
pellets - by polymerising monomer mixt in aq
medium, adding water-soluble catalyst at specified
polymerisation per cent, then adding inhibitor

PATENT-ASSIGNEE: NIPPON ZEON KK[JAPG]

PRIORITY-DATA: 1993JP-0093621 (March 29, 1993)

PATENT-FAMILY:

PUB-NO	PAGES	PUB-DATE	
LANGUAGE		MAIN-IPC	
JP 3348459 B2		November 20, 2002	N/A
008	C08F 002/16		
JP 06279505 A		October 4, 1994	N/A
008	C08F 002/00		

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO
APPL-DATE		
JP 3348459B2	N/A	
1993JP-0093621	March 29, 1993	
JP 3348459B2	Previous Publ.	JP 6279505
N/A		
JP 06279505A	N/A	
1993JP-0093621	March 29, 1993	

INT-CL (IPC): C08F002/00, C08F002/16 , C08F020/12

ABSTRACTED-PUB-NO: JP 06279505A

BASIC-ABSTRACT:

Prepn. of acrylate polymer pellets comprises polymerisation
of a monomer mixt.
contg. 1-8C alkyl acrylate and/or methacrylate in an aq.

medium. A
water-soluble catalyst is added to the medium. When
polymerisation is 85% or
more, then a polymerisation inhibitor is added.

The monomer is methyl methacrylate. The water-soluble
catalyst is hydrogen
peroxide, or water-soluble inorganic peroxide such as
potassium or ammonium
persulphate. The polymerisation inhibitor is a phenol cpd.
(e.g. hydroquinone
or p-t-butyl catechol) or organic sulphur cpd. (e.g.
dithiobenzoyl disulphide),
or hydroxylamine cpd. (e.g. N,N-diethylhydroxylamine).

USE/ADVANTAGE - Transparency and thermostability of the
acrylate beads are
improved. The pellets are useful for paste resin.

In an example, deionised water (6000g), sodium alkylbenzene
sulphonate (30g),
lauryl alcohol (30g), benzoyl peroxide (6g) and methyl
methacrylate monomer
(3000g) were stirred and polymerised at 65 deg.C.
Potassium persulphate (10g)
was added when polymerisation was 92%, and t-butylcatechol
(5.0g) was added at
95%. Obtd. reactant of 96% polymerisation was cooled to
give a latex, which
was spray-dried, and pulverised to form pellets of
4.0x10⁶ Mw.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: PREPARATION ALKYL POLYACRYLATE POLYMER PELLET
POLYMERISE MONOMER

MIXTURE AQUEOUS MEDIUM ADD WATER SOLUBLE
CATALYST SPECIFIED
POLYMERISE PER CENT ADD INHIBIT

ADDL-INDEXING-TERMS:

METHACRYLATE! ACRYLATE METHACRYLATE

DERWENT-CLASS: A14

CPI-CODES: A02-A03; A02-C; A04-F06A; A10-B03; A12-S09;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0610U; 1041U ; 1732U ;

PATENT ABSTRACTS OF JAPAN(11)Publication number : **06-279505**(43)Date of publication of application : **04.10.1994**

(51)Int.Cl.

C08F 2/00

C08F 2/00

C08F 20/12

(21)Application number : **05-093621**(71)Applicant : **NIPPON ZEON CO LTD**(22)Date of filing : **29.03.1993**(72)Inventor : **KANAYAMA AKIKATSU****(54) PRODUCTION OF ACRYLATE POLYMER PARTICLE**

(57)Abstract:

PURPOSE: To produce the particle of a low residual monomer content in a high efficiency without impairing the excellent transparency and heat stability.

CONSTITUTION: A process for producing polymer particles by polymerizing an acrylic ester with 1-8C alkyl and/or a methacrylic ester with 1-8C alkyl or a monomer mixture based thereon in an aqueous medium and drying the product, wherein a water-soluble catalyst and then a polymerization inhibitor are added to the reaction system when the conversion reaches 85% or above.

LEGAL STATUS

[Date of request for examination]

03.02.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3348459

[Date of registration]

13.09.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the acrylate system polymer particle characterized by adding a water-soluble catalyst first to the system of reaction, and subsequently adding a polymerization inhibitor when a polymerization invert ratio becomes 85% or more in having dried and obtaining a polymer particle after carrying out the polymerization of the monomer mixture which is mainly concerned with the acrylic ester which has the alkyl group of carbon numbers 1-8 and/or a methacrylic-ester monomer, or this monomer in an aqueous medium.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to improvement of the manufacture method of an acrylate system or a methacrylate system polymer particle [an acrylate (meta) system polymer particle may be called hereafter]. If it says in more detail, this invention relates to the method of manufacturing efficiently an acrylate system with little residual unreacted monomer, or a methacrylate system polymer particle, without spoiling the outstanding transparency and outstanding thermal stability. [0002]

[Description of the Prior Art] Need has been growing as a material which the acrylate system resin obtained by the polymerization in the inside of water media, such as an emulsion polymerization and a detailed suspension polymerization, (meta) gives the mold goods which were excellent in transparency, coloring nature, weatherability, etc. through processing by the plastisol or the organosol, and is replaced with vinyl chloride resin as a dechlorination system resin especially recently. Furthermore, this (meta) acrylate system resin is used, in order to carry out 0.5-20 weight section combination per vinyl-chloride-resin 100 weight section as processing aid in the use of many vinyl-chloride-resin hard processings from the former, to improve the melt viscosity property of vinyl chloride resin, to enlarge elongation at the time of fabrication or to take out the luster on the front face of mold goods. In order to form the dispersing element which has a fluidity by the plasticizer or organic solvent of the amount of specification, it is detailed and a plastisol or the object for organosols, i.e., the resin particle for a paste, requires that it is [whose mean particle diameter is about 0.2-5 micrometers] a globular form mostly. Therefore, the resin particle for a paste is manufactured according to the emulsion polymerization or the detailed suspension polymerization. Moreover, since the vinyl-chloride-resin fine particles which are the main charges of a compounding agent are generally the things of the irregular configuration of porosity with a particle size of 10-300 micrometers, at the time of kneading of a compounding agent, between the particles of vinyl-chloride-resin fine particles, and into pore, it must be easy to scatter and the resin particle used as processing aid is also used with the form which usually carried out grouping of the globular form particle 0.1 micrometers or less according [therefore] to an emulsion polymerization by uniform. By the way, as mentioned above, although the acrylate (meta) system resin has been used widely, the unreacted monomer which it originated that these polymers have good compatibility with the monomer, and remained to the resin at the time of hot forming vaporized, the odor was emitted, a work environment is polluted or the problem on which goods value is reduced for the odor of mold goods has occurred. Conventionally, the method (JP,60-229902,A) of repeating the operation which adds a radical initiator in a latex at the time of an emulsion-polymerization end as the technique of carrying out removal reduction of the residual monomer of an acrylic (meta) resin is proposed. However, this method requires the great amount of radical initiators and the great processing time, in order to fully reduce the amount of survival of an unreacted monomer, and it has the fault which causes the fall of quality aggravation of thermal stability, weatherability, etc., or productivity. In addition, various methods are proposed. For example, there is the method (JP,63-175086,A) of adding in a polymer solution by making an unreacted monomer, and existing reactant vinyl acetate and reactant methyl acrylate into a scavenger at the time of a solution polymerization end. However, this method is unsuitable, when it is the heterogeneous system which the polymer particle is distributing in a water medium like [an effect is not demonstrated and] the emulsion polymerization in the invention in this application, or a detailed suspension polymerization, if it is not a homogeneous system like solution polymerization. There is a method (JP,46-26975,B) of heat-treating the particle obtained according to the suspension polymerization in the solution of hydroxylation alkali metal or hydroxylation alkaline earth metal in others. However, the top where this method also has inadequate removal of an unreacted monomer, since a particle serves as a floc of a firm irregular configuration and becomes hyperviscosity in the case of the resin for a paste, it is unsuitable. Furthermore, the method (JP,52-17555,A, JP,59-45310,A) of decompressing to 50 or less mmHgs and vaporizing them is proposed, fusing a polymer at 250-290 degrees C in a vent extruder. However, although it is good for manufacturing a pellet since a polymer fuses this method, its particle shape is unsuitable for the important above-mentioned use. By the way, if it heats to an acrylate (meta) system resin, depolymerization will be started to it, and it has the fault of being easy to be decomposed into an acrylic-ester (meta) monomer. Paying attention to this point, the proposal is made by carrying out depolymerization activation energy to beyond a fixed value about the thermoplastic polymer by which heat-resistant resolvability has been improved (JP,60-58408,A, JP,60-58409,A). However, this polymer is a special thing including the specific ring structure unit, and cannot be used suitable for the above-mentioned general use.

[0003]

[Problem(s) to be Solved by the Invention] this invention is the thing of such a situation and is made for the purpose of offering the method of manufacturing efficiently the acrylate system which can prevent the depolymerization by (2) heating which can be suitably used as the object for (1) paste, or an object for processing aid and in which the unreacted monomer which remains in (3) particles has properties, such as being few, or a methacrylate system polymer particle.

[0004]

[Means for Solving the Problem] In order that this invention person may attain the aforementioned purpose, as a result of repeating research wholeheartedly, when carrying out the paste technique of the (1) (meta) acrylate system resin, While the unreacted monomer which remained in this resin vaporizes by heating and heating time of this increases, that it is remarkable a bird clapper and the phenomenon of (2) ** (1) (Meta) When an acrylate system resin was heated, it traced originating in depolymerization (decomposition of a polymer) starting bordering on some temperature conditions. And further, in order to stop the depolymerization by heating of (3) (meta) acrylate system resin It is effective to raise the depolymerization start temperature of this resin, and the amount of the acrylate (meta) system monomer which remains to the mold goods using this resin by this is reduced. Furthermore, in order to attain that the fall of the average degree of polymerization of the acrylate (meta) system resin in these mold goods and weight average molecular weight can be suppressed, and (4) ** (3) Effective, when a water-soluble catalyst is added first and a polymerization inhibitor is subsequently added, after becoming a fixed polymerization invert ratio, in case the polymerization of the acrylate system monomer is carried out in a water medium, (Meta) (5) The depolymerization start temperature of an acrylate (meta) system resin could be raised with ** (3) and the cure of (4), and it found out that the odor which generates this resin after heating processing as a result could be suppressed. this invention is completed based on this knowledge. That is, this invention offers the manufacture method of the acrylate system polymer particle characterized by adding a water-soluble catalyst first to the system of reaction, and subsequently adding a polymerization inhibitor, when a polymerization invert ratio becomes 85% or more in having dried and obtaining a polymer particle, after carrying out the polymerization of the monomer mixture which makes a subject the acrylic ester which has the alkyl group of carbon numbers 1-8 and/or a methacrylic-ester monomer, or this monomer in a water medium.

[0005] Hereafter, this invention is explained in detail. In this invention, the polymerization of the monomer mixture which makes a subject the acrylic ester which has the alkyl group of carbon numbers 1-8 and/or a methacrylic-ester monomer, or this monomer is carried out according to an emulsion polymerization, a detailed suspension polymerization, etc. into a water medium. As this acrylic ester or a methacrylic ester For example, methyl acrylate, ethyl acrylate, n-propylacrylate, Isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, t-butyl acrylate, n-hexyl acrylate, Cyclohexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, Methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, Isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, t-butyl methacrylate, n-hexyl methacrylate, Cyclohexyl methacrylate, 2-ethylhexyl methacrylate, n-octyl methacrylate, etc. are mentioned, and one sort of these may be used and may be used combining two or more sorts. A desirable thing is methyl methacrylate among these acrylic esters or a methacrylic ester.

[0006] The above-mentioned monomer can be made to contain the aforementioned monomer and other monomers which can be copolymerized according to a request. In this case, the content of other monomers is chosen in the range which becomes 50 or less % of the weight to the monomer total quantity. The functional-group content unsaturation monomer for raising the adhesive property of a plastisol constituent etc. as other monomers in which this copolymerization is possible, for example, Specifically Polymerization nature diene series, such as a butadiene and an isoprene, glycidyl (meta) acrylate, The polymerization nature unsaturated compound which has epoxy groups, such as 3, 4-epoxycyclohexyl methyl (meta) acrylate, and a cyclohexene monochrome oxide An acrylic acid, a methacrylic acid, an ETAKURIRU acid, a maleic acid, a fumaric acid, The polymerization nature unsaturated compound which has carboxyl groups, such as itaconic acids and these acid anhydrides 2-aminoethyl (meta) acrylate, 2-aminopropyl (meta) acrylate, 3-aminopropyl (meta) acrylate, 2-amino butyl (meta) acrylate, 3-amino butyl (meta) acrylate, 4-amino butyl (meta) acrylate, An acrylamide, an N-2-aminoethyl (meta) acrylamide, (Meta) Amino-group content polymerization nature unsaturated compounds, such as an N-2-aminopropyl (meta) acrylamide and an N-3-aminopropyl (meta) acrylamide, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 3-hydroxypropyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, 3-hydroxy butyl (meta) acrylate, 4-hydroxy butyl (meta) acrylate, Hydroxyl-group content polymerization nature unsaturated compounds, such as dipentaerythritol hexa (meta) acrylate, In addition, vinylidene compounds, such as aromatic vinyl compounds, such as vinyl esters, such as vinyl acetate and a propionic-acid vinyl, styrene, and an alpha methyl styrene, a vinylidene chloride, and a fluoride vinylidene, etc. are mentioned. One sort of other monomers in which these copolymerization is possible may be used, and may be used combining two or more sorts.

[0007] Especially the molecular weight of the polymer obtained in this invention is not restricted, but weight average molecular weight is usually in the range of 100000-15 million preferably at the range of 200000-10 million. In this invention, when a polymerization invert ratio becomes 85% or more in carrying out the polymerization of this monomer in an aquosity medium, it is required to add a water-soluble catalyst first to the system of reaction, to add a polymerization inhibitor subsequently, and to complete a polymerization. This water-soluble catalyst is used in order to promote the reaction of an unreacted isolation monomer. As this water-soluble catalyst used in this invention, the combination of a hydrogen peroxide, a water-soluble inorganic peroxide, or a water-soluble reducing agent and organic peroxide is mentioned. Potassium persulfate, an ammonium persulfate, etc. are mentioned as an example of a water-soluble inorganic peroxide. Even if it uses one sort of these water-soluble inorganic peroxides, two or more sorts may be combined and it may use, and the amount used is usually chosen in the range of the 0.01 - 0.04 weight section per [to be used] monomer 100 weight section. The reducing agent used

for water as a water-soluble reducing agent, for example as a meltable usual radical oxidation reduction polymerization-catalyst component, For example, ethylenediaminetetraacetic acid or its sodium salt, and potassium salt, Or the complex compound, the sulfinic acid or its sodium salt, and potassium salt of these and heavy metal, such as iron, copper, and chromium L ascorbic acid or its sodium salt, potassium salt, a calcium salt, The first iron of a pyrophosphoric acid, a ferrous sulfate, a ferrous ammonium sulfate, a sodium sulfite, sodium hydrogen sulfite, formaldehyde sodium sulfoxylide, and reducing sugars are mentioned, and one sort of these may be used and may be used combining two or more sorts. Moreover, as organic peroxide, hydroperoxides, such as a cumene hydroperoxide, p-cymene hydroperoxide, t-butyl isopropylbenzene hydroperoxide, a diisopropylbenzene hydroperoxide, p-menthonaphtene hydroperoxide, a decalin hydroperoxide, t-amyl hydroperoxide, tert butylhydroperoxide, and an isopropyl hydroperoxide, are mentioned, for example, and one sort of these may be used and may be used combining two or more sorts. The amount of this organic peroxide used is chosen in the range of per [which is usually used] monomer 100 weight section and the 0.002 - 0.02 weight section. These are used together with the above-mentioned water-soluble reducing agent, and the amount used doubled with this reducing agent is usually chosen in the range of the 0.01 - 0.04 weight section per [to be used] monomer 100 weight section.

[0008] In this invention, the polymerization invert ratio of a monomer performs addition of this water-soluble catalyst preferably 85% or more in the middle of the reaction between 90 - 98%. Under the present circumstances, polymerization temperature is made into about 65-70 degrees C, and the whole system is desirably agitated after addition. Churning time is made into less than 1 hour at this time. An unreacted isolation monomer is consumed in a polymer by this, and the reaction of this isolation monomer can be completed early. If this water-soluble catalyst is added before a polymerization invert ratio becomes 85%, since a reaction overruns recklessly, the thing of predetermined molecular weight will no longer be obtained, and also the character of a latex, i.e., the configuration of the polymer particle after dryness, is confused. On the other hand, it is a book, when it adds, after exceeding 98%. In this invention, after decreasing an unreacted monomer, in order to make the depolymerization at the time of processing suppress further by addition of a water-soluble catalyst in this way, it is required for the last of polymerization reaction to add a polymerization inhibitor. As a polymerization inhibitor used in this invention, organic sulfur compounds, such as hydroxylamine compounds, such as phenolic compound [, such as hydroquinone and a p-t-butyl catechol,], N, and N-diethylhydroxylamine and N-oximido phenyl-hydroxylamine ammonium salt (cupferron), dithio benzoyl disulfide, and a tetraethylthiuram disulfide, etc. are mentioned, for example. One sort of these may be used and may be used combining two or more sorts. In this invention, you may use together and use a polymerization retarder with this polymerization inhibitor. As such a polymerization retarder, the cycloalkene compound of the carbon numbers 5-8, such as a cyclopentene, a cyclohexene, and a cyclo octene, etc. is mentioned, for example, and one sort of these may be used and may be used combining two or more sorts. In the aforementioned polymerization inhibitor and a polymerization retarder, the cycloalkene compound of carbon numbers 5-8 has a desirable phenolic compound as a polymerization retarder as a polymerization inhibitor from the point that the thermal stability of the polymer obtained becomes good. Especially suitable things are t-butyl catechol and a cyclohexene. In this invention, the polymerization invert ratio of a monomer performs preferably addition of the polymerization retarder used together with this polymerization inhibitor or it 85 to 99% in the middle of the reaction between 95 - 98%. Although the amount used is usually chosen in the twice or twice [** mol] as many 0.5-mol range of the below-mentioned amount of polymerization initiators as this, mol-double-adding, such as this polymerization initiator, is preferably good. Thereby, generation of the acrylate system monomer by the depolymerization (meta) of the polymer at the time of heating processing at the temperature of 100-200 degrees C can be suppressed. If this polymerization inhibitor (or polymerization retarder used together with it) is added before a polymerization invert ratio becomes 85%, in order for the polymerization reaction itself to stop, only the polymer in which the unreacted isolation monomer remained mostly is obtained. Consequently, vaporization of the acrylate (meta) system monomer at the time of carrying out heating processing of this polymer becomes intense, and is not desirable practically. [0009] In this invention, when a polymerization invert ratio becomes 85% or more, it is accepted by adding a water-soluble catalyst first and adding the postpolymerization inhibitor (or polymerization retarder used together with it), and an acrylate system polymer particle with little (meta) remains monomer is obtained. In this polymer particle, the radical of the polymerization initiator which remains in a polymer particle in the case of heating at the time of processing works to an unreacted isolation monomer, the radical of this monomer occurs, the weak coupling portion in a molecule is cut by these radicals, and it is thought that depolymerization starts. In this invention, after an unreacted isolation monomer is consumed by addition of a water-soluble catalyst, when a polymerization inhibitor (or polymerization retarder used together with it) carries out the uptake of the above-mentioned polymerization initiator radical, depolymerization is suppressed and it is thought that odor generating at the time of hot forming can be prevented. When a water-soluble catalyst and addition sequence of a polymerization inhibitor (or polymerization retarder used together with it) are made reverse, in order to delay the polymerization reaction itself and to stop by the case, only the polymer in which the unreacted isolation monomer remained mostly is obtained. Moreover, although it is effective in consumption of an unreacted isolation monomer when only this water-soluble catalyst is used, it does not contribute to suppression of depolymerization. On the other hand, when only a polymerization inhibitor (or polymerization retarder used together with it) is used, after the unreacted isolation monomer has remained mostly, polymerization reaction stops. Moreover, since removal of this isolation monomer in a dryness process is difficult, it is difficult to obtain a polymer with few amounts of survival of an unreacted isolation monomer. If heating processing of this polymer is carried out, since both the monomers generated by this isolation monomer and depolymerization will vaporize, generating of an odor becomes remarkable and is not desirable practically. In this invention, this polymer particle is manufactured by the polymerization in the inside of the aquosity medium represented by an emulsion-polymerization method and the detailed

suspension-polymerization method. It is said that an emulsion-polymerization method is the method of carrying out the polymerization of the monomer under existence of an emulsifier and a water-soluble radical initiator, and progresses by the following mechanism. First, a monomer solubilizes to the micell in which the emulsifier met and was formed, the radical of the radical initiator origin generated underwater reaches here, and a polymerization is started. Subsequently, a monomer diffuses at the place of the polymerization of a micell from the emulsified liquid drop of a monomer, a polymerization progresses, and a polymer particle *****s. Furthermore, a micell collapses at the time of a certain invert ratio, and an emulsifier sticks to a polymer particle chiefly and carries out protection stabilization of the particle. Since a new particle is hardly generated after it, future polymerizations serve as a distribution of the particle size which it was carried out on the front face of a polymer particle, therefore was finally approximated.

[0010] In this invention, an emulsion polymerization also includes a seeding emulsion polymerization. Hereafter, an emulsion-polymerization method and a seeding emulsion-polymerization method are explained. The describing [above] emulsion-polymerization method is the method of carrying out the polymerization of the monomer which contains an acrylic ester (meta) in the aquosity medium containing an emulsifier and a polymerization initiator. As this emulsifier, the combination of an anionic surfactant, or an it and a Nonion nature surfactant is usually used. As an anionic surfactant, the well-known thing usually used for an emulsion polymerization, for example, alkylbenzene sulfonates, an alkyl sulfonate, an alkyl-sulfuric-acid ester salt, a fatty-acid metal salt, a polyoxy alkyl ether sulfate salt, a polyoxyethylene carboxylate sulfate salt, a polyoxyethylene-alkyl-phenyl-ether sulfate salt, a succinic-acid dialkyl ester sulfonate, etc. are mentioned, and one sort of these may be used and may be used combining two or more sorts. As a Nonion nature surfactant, for example Moreover, polyoxyethylene alkyl phenyl ether, Polyoxyethylene alkyl ether, polyoxyethylene fatty acid ester, Polyoxyethylene sorbitan fatty acid ester, the polyoxyethylene-alkyl-ether glycerol ester of boric acid, Polyoxyethylene-alkyl-ether phosphoric ester, a polyoxyethylene, etc., The polyoxyethylene chain of the compound which has a polyoxyethylene chain in a molecule and has surface activity ability, and the aforementioned compound Oxyethylene, The compound and further for which the copolymer of oxypropylene is substituted A sorbitan fatty acid ester, A fatty-acid glycerol ester, a glycerine fatty acid ester, pentaerythritol fatty acid ester, etc. are mentioned, and one sort of these may be used and may be used combining two or more sorts. About the amount of these surfactants used, an anionic surfactant is chosen in the range of per [which is usually used] monomer 100 weight section and 0.1 - 5 weight section, and a Nonion nature surfactant is usually chosen in the range of 0 - 5 weight section.

[0011] On the other hand, the thing same as this polymerization initiator as what [what combined a water-soluble inorganic peroxide, or a water-soluble reducing agent and organic peroxide], for example, the thing illustrated in explanation of the above-mentioned water-soluble catalyst, is used. One sort of these water-soluble inorganic peroxides may be used, may be used combining two or more sorts, and are usually used within the limits of 0.0001 - 5 weight section per [to be used] monomer 100 weight section. Moreover, per [which is usually used / 0.001] monomer 100 weight section - within the limits of 5 weight sections, one sort is accepted, and it comes out respectively, or this water-soluble reducing agent and organic peroxide are used combining two or more sorts. In addition, in this emulsion polymerization, in order to promote an operation of the emulsifier and polymerization catalyst which are used, you may use together a higher fatty acid, higher alcohol, mineral, a water-soluble-polymer compound, etc. In this emulsion polymerization, a polymerization is usually performed in the temperature of the range of 30-80 degrees C. Thus, the latex which the copolymer particle whose particle diameter is about 0.03-0.7 micrometers distributed homogeneously is obtained. As for this latex, well-known processing of a salting-out or spray drying is usually performed, and a polymer is taken out as a solid. The molecular weight of this polymer is suitably adjusted by reaction temperature and the molecular weight modifier according to the purpose. On the other hand, a seeding emulsion-polymerization method is a method of making the hypertrophy polymerization reaction of a particle performing in an aquosity medium using the polymerization initiator which consists of the combination of the emulsifier which consists of the combination of the aforementioned anionic surfactant, or an it and a Nonion nature surfactant by using as a nucleus the resin particle prepared by the describing [above] emulsion-polymerization method and the aforementioned water-soluble inorganic peroxide, or the aforementioned water-soluble reducing agent and organic peroxide. Under the present circumstances, the path of the nuclear particle used is usually in the range of an average of 0.03-0.7 micrometers, and the amount used is usually chosen in the range of 1 - 50 weight section per [to be used] monomer 100 weight section. Moreover, the amount of an emulsifier and the polymerization initiator used is the same as that of the case of the describing [above] emulsion-polymerization method. [0012] Next, if one example with a suitable seeding emulsion-polymerization method is explained, after preparing the aquosity emulsion of a desired resin nuclear particle first, the aforementioned water-soluble reducing agent and a monomer are taught and warmed to this, and it holds in temperature of about 30-80 degrees C. On the other hand, the aquosity emulsion and the aforementioned emulsifier solution of organic peroxide are separately prepared using the aforementioned emulsifier, and it supplies to the aquosity emulsion which contains a resin nuclear particle, an aforementioned water-soluble reducing agent, and an aforementioned monomer for these continuously, usually holding the temperature of the range of 30-80 degrees C, and polymerization reaction is performed. In addition, in this seeding emulsion polymerization, in order to promote an operation of the emulsifier and polymerization catalyst which are used, you may use together a higher fatty acid, higher alcohol, mineral, a water-soluble-polymer compound, etc. This copolymer is taken out from the emulsion which contains the particle of 0.2-5 micrometers of mean particle diameters obtained by doing in this way after a polymerization-reaction end as a solid like the case of the aforementioned emulsion polymerization. The molecular weight of this copolymer is suitably adjusted by reaction temperature, the molecular weight modifier, etc. according to the purpose. A detailed suspension-polymerization method is the method of keeping a monomer oil droplet detailed and carrying

out a suspension polymerization, for example, is a way adjust the particle size of a monomer oil droplet beforehand, and it carries out a homogeneous distribution polymerization by homogenization before a polymerization start, using an oil-soluble catalyst as a catalyst. An oil-soluble radical initiator is used as an oil-soluble catalyst. as this oil-soluble radical initiator For example, dibenzoyl peroxide, G 3 and 5, 5-trimethylhexanoylperoxide, Diacyl peroxide, such as JIRAU roil peroxide, diisopropyl peroxy dicarbonate, Peroxy dicarbonate, such as G sec-butylperoxy dicarbonate and G 2-ethylhexyl peroxy dicarbonate Peroxy ester, such as t-butylperoxy pivalate and t-butylperoxy neo decanoate Or organic peroxide, such as acetyl cyclohexyl sulfonyl peroxide and JISAKUSHI nick acid peroxide, Azo compounds, such as - azobis-2-methyl butyronitrile, and further 2, 2'-azobisisobutyronitril, 2, and 2 '2, 2'-azobis dimethylvaleronitrile, etc. can be used. These catalysts can be used combining one sort or two sorts or more, and although the amount used is suitably chosen by a kind, an amount, a brewing method, etc. of a monomer, it can usually be chosen in the range of per use monomer 100 weight section and the 0.001 - 5.0 weight section.

[0013] Moreover, in a detailed suspension-polymerization method, the combination of an anionic surfactant, or an it and a Nonion nature surfactant is used as a surfactant. It is ***** with same what was illustrated by the aforementioned emulsion-polymerization method as this surfactant and thing of the same kind. Moreover, you may add an emulsification assistant for the purpose of protection stabilization of the emulsified liquid drop of the monomer obtained by homogenization. As an emulsification assistant of this purpose, the fatty acid ester of the higher alcohol which has the alkyl group of carbon numbers 10-24, the higher fatty acid of carbon numbers 10-20, and the higher alcohol of carbon numbers 4-18 and the higher fatty acid of carbon numbers 4-8 etc. is used. the amount of the emulsification assistant used -- per [0] monomer 100 weight section - 5 weight sections -- it is 0.5 - 2 weight section preferably In this detailed suspension-polymerization method, the premix of polymerization assistants used into an aquosity medium according to the aforementioned oil-soluble catalyst, a monomer, the aforementioned surfactant, and a request, such as higher fatty acids and higher alcohol, and the other additives is added and carried out first, it homogenizes with a homogenizer, and particle-size regulation of an oil droplet is performed. As this homogenizer, the high-pressure jet from a colloid mill, a vibratory mixer, two-step formula high pressure pumping, a nozzle, or an orifice, ultrasonic churning, etc. are mentioned, for example. Furthermore, although regulation of the particle size of an oil droplet is influenced with control of the shearing force at the time of homogenization, the churning conditions under polymerization, the form of a reactor, the amount of a surfactant or an additive, etc., these can choose suitable conditions by easy preliminary experiment. Next, the liquid which it homogenized by doing in this way is sent to a polymerization can, a temperature up is carried out, agitating slowly, a polymerization is usually performed in the temperature of the range of 30-80 degrees C, and the latex of the latus resin particle of a particle size distribution is obtained for the first an average of] particle size by 0.5-3 micrometers. As for this latex, well-known processing of spray drying etc. is usually performed, and a polymer is taken out as a solid. The molecular weight of this polymer is suitably adjusted by reaction temperature and the molecular weight modifier according to the purpose.

[0014] Into an aquosity medium, a suspension-polymerization method makes a monomer oil droplet suspend under existence of a dispersant, it is the method of carrying out the polymerization of the monomer in this oil droplet, and an oil-soluble catalyst is used for it as a catalyst. The kind and the amount of the oil-soluble catalyst used which are used here are the same as that of the case of the aforementioned detailed suspension-polymerization method. As this dispersant, polyvinyl alcohol (PVA), a carboxymethyl cellulose (CMC), a hydroxyethyl cellulose (HEC), a methyl cellulose (MC), gelatin, an alginic acid, sodium polyacrylate, a polyacrylamide, phosphoric-acid hydrogen NINATORIUMU, a polyethylene oxide, etc. can be used, for example. One sort of these dispersants may be used, you may use combining two or more sorts, and the amount used is usually chosen in the range of per use monomer 100 weight section and the 0.001 - 2.0 weight section. The other additives used into a water medium according to the aforementioned oil-soluble catalyst, a monomer, the aforementioned dispersant, and a request are added first, and a monomer oil droplet is made to form in this suspension-polymerization method. Then, after carrying out a temperature up, agitating the whole system in which this oil droplet was formed, in the temperature of the range of 30-80 degrees C, a polymerization is usually performed. By the above-mentioned method, the particle whose mean particle diameter is 10-200 micrometers is manufactured. The molecular weight of this particle is suitably adjusted by reaction temperature and the molecular weight modifier according to the purpose. The polymer particle obtained by this invention is dried after being manufactured by the polymerization, i.e., the emulsion-polymerization method, the seeding emulsion-polymerization method, detailed suspension-polymerization method, or suspension-polymerization method in the inside of the above-mentioned water medium. In addition, the particle for a paste can be obtained by grinding, if spray drying of the latex obtained by the seeding emulsion polymerization or the detailed suspension polymerization is usually carried out and it is required. The processing aid particle for vinyl chloride resin can be obtained by carrying out spray drying of the emulsion-polymerization latex, or solidifying and carrying out after [dehydration] fluidized drying. As for the gas with which this dryness is presented, it is desirable that it is inert gas like nitrogen in order to avoid a dust explosion. In addition, dryness can be performed by the other various dryness method of the above-mentioned dryness method.

[0015]

[Example] Next, an example explains this invention to a detail further. In addition, this invention is not limited at all by these examples. In the example, the amount of the remains unreacted monomer in resin powder, the weight average molecular weight of a resin polymer, and the mean particle diameter of a resin powder particle were measured by the following methods.

(1) Gas chromatography by measurement Shimadzu Corp. of the amount of remains unreacted monomers in resin powder It is [phix3m of SUS3mm, and] 20% as a column to GC-4PB1TF. Ucon Oil LB-1800X is used and it is Flush about a remains

unreacted monomer. Sample It *****ed from the resin in FLS-1, and supplemented and measured in liquid oxygen.

(2) Weight average molecular weight of a resin polymer (it only considers as average molecular weight below)

Gel-permeation-chromatography SC-8010 by TOSOH CORP. were used, and it measured by the conventional method.

(3) The mean particle diameter of the single particle at the time of the polymerization-reaction end of the measurement resin of the mean particle diameter of resin powder particle size measured the length of about 1000 particles using the 10000 times as many enlargement taken with the transmission electron microscope as this, asked for the average, and was taken as the primary particle mean particle diameter. The secondary particle mean particle diameter containing the floc of the fine particles which carried out spray drying of the latex after a polymerization-reaction end added carbon black 50mg as an antistatic agent to 50g of powder after removing a big and rough particle through the screen of 250 micrometers of openings, performed sieve analysis to the bottom of vibration using the JIS standard sieve, and asked for it as a particle size used as 50 % of the weight. In addition, the resin powder particle size obtained according to the suspension polymerization was measured by the same method as the above-mentioned secondary particle mean particle diameter.

[0016] Teach methyl methacrylate monomer 3000g, agitate and emulsion-size, move to the autoclave of 10L with which this mixture was independently deaerated using the homogeneous machine, and carry out a temperature up to 65 degrees C, after teaching 6g of benzoyl peroxides of lauryl alcohol 30g of 6000g of deionized water, 30g of alkyl benzene sodium sulfonate of an emulsifier, and an emulsification assistant, and a radical initiator to the reactor made from stainless steel of example 110L and carrying out reduced pressure deaeration. The polymerization was started. When it became 92% of polymerization invert ratios, 10g of potassium persulfate was added, the temperature up was carried out to 70 degrees C, and it agitated for 10 minutes. Furthermore, when the polymerization invert ratio became 95%, t-butyl catechol 5.0g was added. And it cooled, when the polymerization invert ratio became 96%, and the polymerization was ended, and it decompressed at 53 degrees C, and when resulting in 300mmHgG, operation of putting in air was repeated. Spray drying of the latex cooled and obtained was carried out with nitrogen, and acrylic paste resin powder (A) was obtained through the trituration process. The average molecular weight of the obtained resin powder (A) was 4.0×10^6 , the amount of remains monomers of resin powder (A) was 0.20 % of the weight, the average of the primary particle at the time of a polymerization-reaction end was 1.1 micrometers, and the average of the mean particle diameter of the secondary particle after spray drying was 25 micrometers. After mixing this resin (powder A) 100 weight section and the tricresyl phosphate 100 weight section as a phosphoric ester system plasticizer with an Ishikawa style RAIKAI machine, reduced pressure degassing processing was performed and the acrylic paste sol was obtained. The obtained sol was supplied to the mould made from aluminum (10x20x2mm convex type), and it heated in hot blast circulating oven on the conditions shown in the 1st table. Then, after taking out the mould and cooling at a room temperature, the remains monomer in mold goods and measurement of average molecular weight were performed like resin powder (A). The result is shown in the 1st table.

In example of comparison 1 example 1, except having made reverse injection sequence of potassium persulfate and t-butyl catechol, resin powder and the sol were created like the example 1, and evaluation of measurement of a mean particle diameter, the amount of remains monomers, and average molecular weight was performed. The result is shown in the 1st table. In example of comparison 2 example 1, except having not supplied potassium persulfate, resin powder and the sol were created like the example 1, and evaluation of measurement of a mean particle diameter, the amount of remains monomers, and average molecular weight was performed. The result is shown in the 1st table.

In example of comparison 3 example 1, except having not supplied t-butyl catechol, resin powder and the sol were created like the example 1, and evaluation of measurement of a mean particle diameter, a remains monomer, and average molecular weight was performed. The result is shown in the 1st table.

In example of comparison 4 example 1, except both having not supplied potassium persulfate and t-butyl catechol, it carried out like the example 1, resin powder and the sol were created, and evaluation of measurement of a mean particle diameter, the amount of remains monomers, and average molecular weight was performed. The result is shown in the 1st table.

In example of comparison 5 example 1, when it became 80% of polymerization invert ratios, and 10g of potassium persulfate was added, the temperature up was carried out to 70 degrees C and it agitated for 10 minutes, since temperature became high too much, the polymerization was stopped, and creation of resin powder and a sol was not performed.

Phosphoric-acid hydrogen NINATORJUMU 180g of 6000g of deionized water, 60g of sodium polyacrylate of a dispersant, and a distributed assistant, azobisisobutyronitril 39g of a radical initiator, and methyl methacrylate monomer 3000g were taught to the reactor made from stainless steel of example 210L, the temperature up was carried out to 78 degrees C, and the polymerization was started. When the polymerization invert ratio became 93%, 10g of potassium persulfate was added, and it agitated for 10 minutes. When the polymerization invert ratio furthermore became 95%, t-butyl catechol 5g was added. And it cooled, when the polymerization invert ratio became 96%, and the polymerization was ended. The suspension cooled and obtained was filtered, and it rinsed, dried, and resin (powder B) 2460g was obtained. The average molecular weight of the obtained resin powder (B) was 4.2×10^6 , the amount of remains monomers of resin powder (B) was 0.22 % of the weight, and the mean particle diameter was 100 micrometers. This resin powder (B) 10g was heated in hot blast circulating oven at 190 degrees C. Then, after taking out resin powder (B) and cooling at a room temperature, the remains monomer in resin powder and measurement of average molecular weight were performed like resin powder (A). The result is shown in the 1st table.

[0017]

[Table 1]

第1表-1

	樹脂粉末		樹脂粉末粒径	
	残留単量体 (wt%)	平均分子量	1次粒子平均粒径 (μm)	2次粒子平均粒径 (μm)
比較例1	2.50	4.2×10^6	1.1	27
比較例2	1.20	4.1×10^6	1.3	25
比較例3	0.80	3.9×10^6	1.2	25
比較例4	1.10	4.0×10^6	1.1	27
実施例1	0.20	4.0×10^6	1.1	25
実施例2	0.22	4.2×10^6	100 (μm)	

[0018]

[Table 2]

第1表-2

	成形品 (厚さ1.0mmシート)					
	150℃×5分		170℃×5分		190℃×5分	
	残留単量体 (wt%)	平均分子量	残留単量体 (wt%)	平均分子量	残留単量体 (wt%)	平均分子量
比較例1	1.10	4.2×10^6	1.60	3.7×10^6	1.90	3.5×10^6
比較例2	0.60	3.5×10^6	0.70	3.0×10^6	0.90	2.2×10^6
比較例3	0.90	3.0×10^6	1.60	2.2×10^6	6.20	6.2×10^5
比較例4	0.80	3.6×10^6	1.20	3.2×10^6	3.00	8.0×10^5
実施例1	0.05	3.9×10^6	0.06	3.9×10^6	0.10	3.9×10^6
実施例2	—	—	—	—	0.10 ¹⁾	4.0×10^6 ¹⁾

[0019] notes 1) More than resin powder, an acrylate system polymer particle with little (examples 1 and 2) and a residual unreacted monomer can be obtained by using this invention method so that clearly. On the other hand, in the example 1 of comparison which changed a water-soluble catalyst and the preparation sequence of a polymerization inhibitor, the examples 2 and 3 of comparison only using either, and the example 4 of comparison which did not use both, only the acrylate system polymer particle with much residual unreacted monomer was able to be obtained. Moreover, in the example 5 of comparison which added the water-soluble catalyst before the polymerization invert ratio became 85%, obtaining an acrylate system polymer particle itself was not completed.

[0020]

[Effect of the Invention] According to this invention, an acrylate system polymer particle with little residual unreacted monomer can be manufactured efficiently. Therefore, the acrylate system polymer particle which removed the unreacted monomer can be suitably used as the object for a paste, or an object for processing aid in the state as it is. Moreover, the acrylate system polymer particle by which the unreacted monomer was mitigated by this invention method is used suitable for the aforementioned use also from excelling in transparency, thermal stability, etc.

[Translation done.]